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Modified epoxy resin composition and process for the preparation thereof.

Modified epoxy resin composition having excellent flexibility and excellent compatibility with conventional epoxy resins as well as the original properties of the epoxy resin before modified such as mechanical strength, adhesion, heat resistance and chemical resistance, which is obtained by treating an epoxy resin with at least one modified adduct [D] of a conjugated diene polymer or copolymer which has an imido bond and/or amido bond and a semi-ester structure and has an acid value owing to a free carboxyl group of 5 to 100, the modified adduct being obtained by reacting an adduct [A] of a polymer of a conjugated diene having a number average molecular weight of 300 to 20,000 or a copolymer of the conjugated diene and a vinyl monomer with an α,β -unsaturated dicarboxylic acid or its anhydride, with a compound [B] containing one primary amino group in the molecule and a compound [C] containing a hydroxy group in the molecule.

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MODIFIED EPOXY RESIN COMPOSITION AND PROCESS
FOR THE PREPARATION THEREOF

The present invention relates to a modified epoxy resin composition and to a process for modifying an epoxy resin in order to provide it with other properties without making the original properties thereof.

5 Epoxy resins usually have excellent properties, such as excellent mechanical strength, adhesion, heat resistance and chemical resistance, and hence, they are widely used for making coating compositions, electrical insulators, materials for civil engineering and construction, adhesives and
10 composite materials. However, the cured epoxy resin products usually possess and inferior flexibility, and hence, attempts have been made to improve the fragility thereof and to give them excellent impact resistance and thermal shock resistance. For example, it
15 has been proposed to modify the epoxy resin by adding thereto a modifying agent such as a polysulfide, polychloroprene, polybutadiene, dimeric acid, polyester ether or polyamide, but such methods have some disadvantages that result in a deterioration of the original
20 properties of epoxy resin such as mechanical strength, electric properties, heat resistance, solvent resistance, corrosion resistance, and furthermore that the most suitable method must be individually selected in accordance with the intended utilities. When employing the resin for
25 making coating compositions, the epoxy resin should have impact

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resistance and an adhesion to the substrate as well as solvent resistance, and corrosion resistance. Furthermore, other properties are required such as compatibility of the epoxy resin with the modifying agent, homogeneity, film-forming properties of the vehicle resin and crosslinking curing properties. Such requirements have never been satisfied by the known techniques.

Recently, epoxy resins have been used as materials for cathode electrocoating composition suitable for coating automobiles, and for this use various methods have been proposed for improving the properties of the epoxy resins, in order to give coating compositions having excellent chip resistance, corrosion resistance, etc., Among these, it has been proposed to use as a flexibilizer a liquid polybutadiene which has been used for the preparation of anode electrocoating compositions. However, the liquid polybutadiene has an insufficient compatibility with the epoxy resin, and even if it is chemically bonded to the epoxy resin by means of an appropriate reactive group, it is still difficult to obtain a good composition which can give a clear uniform coating layer. In order to eliminate such a drawback, particularly to improve the compatibility of the flexibilizer with the epoxy resin, various methods have been proposed. For example, it is disclosed in Japanese Patent Publication (unexamined) No. 97632/1979 that a base resin for a cationic electrocoating composition is obtained by reacting a butadiene-acrylonitrile copolymer containing

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carboxyl groups at both ends thereof with an epoxy resin. According to this method, the compatibility with the epoxy resin is much improved owing to the acrylonitrile group, but it still has insufficient film-forming properties and flexibility. Moreover, since this copolymer is a comparatively high molecular weight functional polymer, use thereof is restricted. For example, it is necessary to specify the ratio of the copolymer to the epoxy resin in order to give the desired homogeneity of the electrocoating composition or to regulate the concentration of a cationic group in order to give the desired electrophoresis. This method is also disadvantageous in view of the high cost.

Another approach for improving the flexibility by using a liquid polybutadiene is disclosed in Japanese Patent Publication (unexamined) No. 5933/1980, wherein a reaction product of an epoxy resin with a conjugated diene polymer containing a carboxyl group at the end or intermediate of the molecule is used as a base resin for a cationic electrocoating composition. The liquid polybutadiene used in this method is substantially a liquid polybutadiene having a high 1,2-vinyl structure and having carboxyl groups at both ends thereof, and the liquid polybutadiene is used for improving smoothness and curing properties of the coating film. These liquid polybutadienes having a high 1,2-vinyl structure or consisting mainly of butadiene skeleton are still inferior in their compatibility with the epoxy resins.

Another method is proposed in Japanese Patent Publication (unexamined) No. 5932/1980 which discloses a resin composition suitable for a cathode precipitating type electrocoating which comprises

5 predominantly a reaction product of a basic resin and an amine-modified epoxy resin, wherein the basic resin is obtained by reacting an anhydrous maleic acid adduct of a liquid polybutadiene or a natural drying oil with a diamine containing a tertiary amino group within the

10 molecule (e.g. N,N-dimethylaminopropanediamine) and an aminoalcohol (e.g. monoethanolamine) or a diamine containing a hydroxy group (e.g. 2-(N,N-dihydroxymethylamino)ethylamine), by which the liquid polybutadiene or natural drying oil is bonded to a tertiary amino group and

15 hydroxy group via an imidohydrocarbon bond. Since the basic resin used in this method contains a large amount of an aliphatic tertiary amino group having a comparatively strong basicity and having a polymerization catalyst activity to the epoxy group, when the basic resin is reacted with the epoxy

20 resin in a system containing an excess amount of epoxy groups, a polymerization reaction due to ring-opening of the epoxy groups occurs and the esterification reaction between the carboxyl group of the basic resin and the epoxy group of the epoxy resin proceeds insufficiently, which unfavorably results in

25 gelation of the system. Accordingly, in the method of Japanese Patent Publication (unexamined) No. 5932/1980, the amination of the epoxy resin

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is carried out while preventing the above-mentioned undesirable side reaction by carrying out the reaction in the presence of an equimolar amount of an amine to the excess epoxy groups, or by charging the basic resin into the system after a part of the amination reaction has taken place.

It has been required to give a flexibility to the epoxy resins not only in the field of cationic electrocoating but also in other coating fields and in the production of carious molding compositions.

We have now developed an improved modified epoxy resin which can give a cured product having excellent flexibility and which has an excellent compatibility with other epoxy resins and an improved process for modifying epoxy resins in order to give them various properties without making the original properties thereof inferior.

Advantages of the present invention will be apparent to those skilled in the art from the following description.

Accordingly, the improved epoxy resin of the present invention is obtained by treating an epoxy resin with at least one modified adduct [D] of a conjugated diene polymer or copolymer which has an imido bond and/or amido bond and a semiester structure and has an acid value owing to a free carboxyl group of 5 to 100, preferably 10 to 50, the modified adduct being obtained by reacting an

adduct [A] of a polymer of a conjugated diene having a number average molecular weight of 300 to 20,000, preferably 500 to 5,000, or a copolymer of the conjugated diene and a vinyl monomer with an α, β -unsaturated dicarboxylic acid or its anhydride, with a compound [B] containing one primary amino group in the molecule and a compound [C] containing a hydroxy group in the molecule.

The modified epoxy resin of the present invention is characteristic in that it has a good compatibility with conventional epoxy resins, such as epi-bis type epoxy resins derived from bisphenol A and epichlorohydrin, polyglycidyl ether type epoxy resins derived from a novalac resin, polyglycidyl amine type epoxy resins derived from an aromatic amine, and polyglycidyl ester type epoxy resins derived from an aromatic polycarboxylic acid, and that when it is used in coating compositions and molding compositions, it can give cured products having excellent flexibility, such as excellent impact resistance and thermal shock resistance.

The present invention is also characteristic in that the most suitable micro structure or molecular weight of the conjugated diene polymer or copolymer can freely be selected in accordance with the requirements and utilities of the final products. For example,, when a liquid polybutadiene being rich in cis-1,4 bonds is used as the base

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of the modified adduct, a comparatively small amount of the modified adduct can give the desired flexibility to the epoxy resin. When an adduct having a high 1,2-vinyl structure is used, a hard composition can be obtained.

- 5 Furthermore, by controlling the amount of the α,β -unsaturated dicarboxylic acid or its anhydride (e.g. maleic anhydride) introduced into the liquid polybutadiene, or by controlling the modifying conditions, the dicarboxylic acid or its anhydride can react with the liquid polybutadiene in an amount equimolar or nearly equimolar to the epoxy resin (as
10 calculated as a monomer).

- The conjugated diene polymer used in the present invention has a number average of from 300 to 20,000, preferably 500 to 5,000. The conjugated diene
15 polymer includes homopolymers of a conjugated diene monomer and also copolymers thereof with other copolymerizable monomers. The micro structure of the double bond thereof is not important, but the polymer contain an optional ratio of 1,4-bonds, 1,2-bonds or 3,4-bonds.

- 20 Suitable examples of the conjugated diene monomer are butadiene, isoprene, chloroprene and 1,3-pentadiene. Suitable examples of other copolymerizable monomers are vinyl monomers such as acrylic acid esters (e.g. methyl acrylate, ethyl acrylate, etc.), methacrylic acid esters
25 (e.g. methyl methacrylate, ethyl methacrylate, etc.),

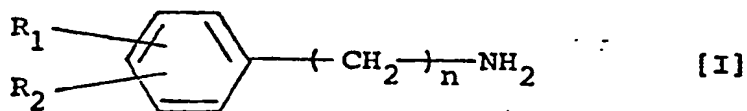
acrylonitrile, styrene, acetylene, ethylene or propylene which may be used alone or in combination of two or more thereof. The conjugated diene copolymer preferably contains 50 % by mole or more of the conjugated diene monomer, preferably butadiene or isoprene. The conjugated diene polymer and copolymer may also contain carboxyl and/or hydroxy groups.

The α, β -unsaturated dicarboxylic acid or its anhydride includes maleic anhydride, maleic acid, fumaric acid, itaconic acid and citraconic acid, amongst which maleic anhydride is particularly suitable. In accordance with variations of the micro structure and molecular weights of the conjugated diene polymer or copolymer, the types of the copolymerizable monomers and also the desired utilities of the final products, the most suitable amount of the α, β -unsaturated dicarboxylic acid or its anhydride and also the most suitable type and amount of the compounds [B] and [C] are carefully selected.

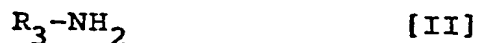
The compound [B] containing one primary amino group in the molecule includes a compound containing a primary amino group and an aromatic residue in the molecule

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which has the following formula:



5 wherein R_1 and R_2 are the same or different and are each hydrogen, an alkyl group having 1 to 5 carbon atoms, halogen, cyano, hydroxy, thiol, methoxy, $-\text{CONH}_2$, $-\text{COCH}_3$, $-\text{COOCH}_3$, or $-\text{N}(\text{CH}_3)_2$, and n is 0 or an integer of from 1 to 3, and a compound containing a primary amino group and an
10 aliphatic or alicyclic hydrocarbon group in the molecule which has the following formula:



wherein R_3 is an aliphatic hydrocarbon group having 1 to 18 carbon atoms or an alicyclic hydrocarbon group having 3 to
15 18 carbon atoms, the aliphatic and alicyclic hydrocarbon groups containing optionally an ether bond.

Suitable examples of the compound of the formula
[I] are aniline, toluidine, xylidine, aminophenol, aminocresol, aminoresorcinol, ethylaniline, cumidine,
20 p-tert-butylaniline, p-tert-amylaniline, benzylamine, phenethylamine, anisidine, aminophenetol, vinylaniline, chloroaniline, dichloroaniline, aminothiophenol, aminobenzonitrile, aminobenzamide, aminoacetophenone, methyl aminobenzoate, aminoethylphenol and N,N-dimethylphenylene-
25 diamine,

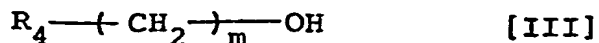
Suitable examples of the compound of the formula [II] are saturated aliphatic amines such as methylamine,

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ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, tert-butylamine, n-amylamine, isoamylamine, tert-amylamine, 1,2-dimethylpropylamine, hexylamine, heptylamine, octylamine, 2-ethylhexylamine, 5 nonylamine, decylamine, laurylamine, tetradecylamine, hexadecylamine, or octadecylamine; unsaturated aliphatic amines such as vinylamine, allylamine, methallylamine, 1-amino-4-pentene, propargylamine, 3-amino-3-methyl-1-butyne, or oleylamine; amines containing an ether group 10 such as 2-aminoethyl ethyl ether, 3-methoxypropylamine, 3-ethoxypropylamine, propoxypropylamine, isopropoxypropylamine, butoxypropylamine, isobutoxypropylamine, 2-ethylhexyloxypropylamine, decyloxypropylamine, lauryloxypropylamine, myristyloxypropylamine, or 15 furfurylamine; alicyclic amines such as cyclopropylamine, cyclopropylmethylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, or alkyl-substituted derivatives thereof.

The compounds [I] and [II] may be used as single 20 compounds, or as a mixture of two or more thereof.

The compound [C] containing a hydroxy group in the molecule includes a compound for the formula:



wherein R_4 is a saturated or unsaturated hydrocarbon group 25 having 1 to 18 carbon atoms; a saturated or unsaturated hydrocarbon group having 1 to 12 carbon atoms and containing

a cyano group, a halogen atom, in ether bond, an ester bond or a hydroxy group which bonds to a secondary or tertiary carbon; a saturated alcohol residue having 1 to 8 carbon atoms; an acrylic acid residue; or a methacrylic acid residue; and m is 0 or an integer of from 1 to 3.

Suitable examples of the compound of the formula [III] are saturated alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, n-amyl alcohol, activated amyl alcohol, isoamyl alcohol, sec-amyl alcohol, 3-pentanol, tert-amyl alcohol, n-hexanol, methylamyl alcohol, 2-ethylbutanol, n-heptanol, 2-heptanol, 3-heptanol, n-octanol, 2-octanol, 2-ethylhexanol, 3,5,5-trimethylhexanol, nonanol, n-decanol, undecanol, n-dodecanol, trimethylnonyl alcohol, tetradecanol, heptadecanol, or octadecanol; unsaturated alcohols such as allyl alcohol, crotyl alcohol, 3-buten-2-ol, propargyl alcohol, or oleyl alcohol; benzyl alcohol, phenethyl alcohol, cinnamyl alcohol, benzyloxyethanol, and their nucleus-substituted derivatives; halogenated alcohols such as ethylene chlorohydrin; ethylene cyanohydrin, furfuryl alcohol, tetrahydrofurfuryl alcohol; glycol monoalkyl ethers such as ethylene glycol monoalkyl ethers, diethylene glycol monoalkyl ethers, triethylene glycol monoalkyl ethers which have 1 to 8 carbon atoms in the alkyl moiety; ethylene oxide adducts such as phenol ethylene oxide adduct, an alkylphenol ethylene oxide adduct, an aliphatic or aromatic monocarboxylic acid ethylene oxide adduct; hydroxyalkyl acrylates or methacrylates such as

2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate,
3-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate;
glycols such as propylene glycol, α -monochloroglycerin,
2-hydroxy-2-methyl-propanol-1; and further glycidol, cyclohexanol,
5 glycerin dichlorohydrin, glycerin di-aliphatic carboxylate,
abiethinol. These compounds may be used alone or as
a mixture of two or more thereof.

The amount of α, β -unsaturated dicarboxylic acid or
its anhydride may vary depending on the molecular weight of
10 the conjugated diene polymer or copolymer to be reacted, but
is usually in an amount such that the content of the α, β -
unsaturated dicarboxylic acid or its anhydride in the adduct
[A] becomes 5 to 50 % by weight, preferably 5 to 30 % by
weight. When the content of α, β -dicarboxylic acid or its
15 anhydride in the adduct [A] is lower than 5 % by weight, the
modified epoxy resin obtained shows an inferior compatibility
with other epoxy resins, and on the other hand, when the
content is over 50 % by weight, the modification reaction can
hardly be carried out because of the increased viscosity of
20 the reaction system.

The adduct [A] of the conjugated diene polymer or
copolymer with the α, β -dicarboxylic acid or its anhydride
can be prepared by any conventional method, for example, by
mixing a conjugated diene polymer or copolymer and
25 an α, β -dicarboxylic acid or its anhydride (e.g. maleic
anhydride) and reacting them under an inert gas at a
temperature of 50 to 300°C, preferably 150 to 210°C, for 30
minutes to 10 hours, preferably 2 to 6 hours. In this

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reaction, an antigelling agent may optionally be added in an amount of 0.01 to 5 % by weight, and further an inert organic solvent may be used.

The modified adduct [D] can be prepared by reacting the adduct [A] with an amino compound [B] of the formula [I] or [II] and a compound [C] containing a hydroxy group, wherein the compound [B] and the compound [C] are used in an amount of 5 to 95 % by mole and 95 to 5 % by mole, respectively, to 1 mole of the α,β -dicarboxylic acid or its anhydride (e.g. maleic anhydride) bonded to the conjugated diene polymer or copolymer. In this reaction, the compound [B] is reacted with the acid or its anhydride group contained in the adduct [A] and is almost all formed into imido bonds, but it may optionally be formed into an amido bond-carboxylic acid skeleton. Besides, the compound [C] is formed into an ester bond - carboxylic acid skeleton.

The modified adduct [D] preferably contains at least 0.5 equivalent weight, preferably 0.75 equivalent weight or more, of a free carboxyl group (as calculated as -COOH number) per one molecule of the conjugated diene polymer or copolymer (as calculated based on the average molecular weight). In this respect, the suitable amounts of the compound [B] and compound [C] are also determined.

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The reaction of the adduct [A] with the compounds [B] and [C] may be carried out simultaneously in the same reaction system or in sequence, that is, by reacting firstly the adduct [A] with the compound [B] or [C] (preferably compound [C]) and adding the compound [C] or [B] (preferably compound [B]) to the reaction system preferably after partially carrying out the above reaction, and then completing the reaction of the adduct [A] and the compounds [B] and [C]. Thus, the reaction of the adduct [A] with the compounds [B] and [C] includes the following features.

(1) The adduct [A] is mixed with the compound [B] and the compound [C] and the mixture is simultaneously subjected to the reaction.

(2) The adduct [A] is firstly, preferably partially, reacted with the compound [C], and subsequently the compound [B] is reacted with the resulting reaction mixture.

(3) The adduct [A] is reacted with the compounds [B] and [C] while adding dropwise a mixture of the compounds [B] and [C] to the reaction system.

(4) The adduct [A] is firstly, preferably partially, reacted with the compound [B], and subsequently the compound [C] is reacted with the resulting reaction mixture.

When the adduct [A] is firstly reacted with an equimolar or excess amount of the compound [C], whole or most acid anhydride groups contained in the adduct [A] are

ring-opened to give a partially esterified product, and then, the extra partial ester bonds may be converted into imido bonds by reacting the product with the compound [B] of a predetermined amount. In this case, the suitable amount of the compound [B] is determined so that the ratio of the substituents in the final product is within a suitable range.

By the reaction of the adduct [A] and the compound [C], a partially esterified product is obtained. This reaction can be carried out by any conventional method, for example, by reacting the adduct [A] with the compound [C] at a temperature of 30 to 200°C, preferably 30 to 160°C, for 30 minutes to 5 hours, usually in the presence of a slight amount of a catalyst selected from quaternary ammonium salts, tertiary amines, alkali metal salts, or organic acids, wherein an inert solvent such as toluene, xylene, methyl isobutyl ketone or ethylene glycol ethyl ether monoacetate may optionally be used.

The reaction of the adduct [A] and the compound [B] may also be carried out by any conventional method, for example, by reacting the adduct [A] or the partial reaction product of the adduct [A] and the compound [C] with the compound [B] at a temperature of 30 to 250°C, preferably 30 to 200°C, whilst removing the by-produced water. Since this reaction is occasionally accompanied with an exotherm or foaming, the compound [B] is added portion wise to the reaction system, or an appropriate inert solvent as mentioned above

is used. In order to obtain partially amidated products, it is preferable to carry out the reaction at a temperature not higher than 100°C.

The finishing point of the above-mentioned reactions may be determined by gas chromatography, IR spectrum, or based upon the amount of the by-produced water, but it is usually easily determined by measuring an acid value, amine value or saponification value of the reaction system.

Modification of an epoxy resin with the modified adduct [D] thus obtained is carried out by mixing an epoxy resin containing at least one epoxy group, preferably two or more epoxy groups with the modified adduct [D] and reacting the mixture under an inert gas at a temperature of 50 to 250°C, preferably 80 to 200°C, for 30 minutes to 10 hours, wherein appropriate catalyst and solvent as mentioned above may optionally be used. The reaction is usually carried out while checking the acid value of the system in order to determine the finishing point.

The amount of the modified adduct [D] may vary with the requirements and utilities of the final modified epoxy resins, but is usually in the range of 5 to 300 parts by weight, preferably 10 to 100 parts by weight, to 100 parts by weight of the epoxy resin.

The modified epoxy resin obtained by the present invention contains an epoxy group in the molecule, and hence, can be used like the conventional unmodified epoxy

resins and can give a cured product having excellent flexibility and thermal shock resistance whilst maintaining excellent mechanical strength, adhesion, heat resistance, and chemical resistance. Thus, the modified epoxy resin of the present invention can be formed into a resin for cationic electrocoating composition having excellent chip resistance and corrosion resistance by aminating the remaining epoxy groups of the modified epoxy resin and also using isocyanate compounds. Furthermore, the modified epoxy resin of the present invention can be used for the preparation of various coating compositions by incorporating it with a suitable curing agent. Moreover, a liquid resin obtained by modifying an epoxy resin having a low molecular weight by the present invention is suitable as a cast resin having an excellent thermal shock resistance.

The present invention is illustrated by the following Examples, but is not limited thereto.

Example 1

A liquid polybutadiene (number average molecular weight: 1680, viscosity at 20°C: 650 cp, iodine value (Wijs method): 445, cis-1,4 structure: 76 %, trans-1,4 structure: 23 %, and 1,2-vinyl structure: 1%) (340 g), maleic anhydride (60 g) and iron naphthenate (Fe: 5.0 %) (0.68 g) are charged into a 500 ml four-necked flask, and the mixture is reacted under nitrogen gas at 190°C for 4 hours to give a maleinated polybutadiene (total acid value: 162).

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Into a 500 ml four-necked flask are charged the maleinated polybutadiene obtained above (200 g), toluene (54.0 g), 2-hydroxyethyl methacrylate (13.0 g), phenothiazine (0.8 g) and benzyltrimethylammonium chloride (30 mg), and the mixture is reacted at 90°C for 2 hours. The flask is equipped with a condenser for taking out the by-produced water and a dropping funnel, and thereto is added dropwise a mixture of aniline (18.6 g), phenothiazine (0.5 g) and toluene (44 g) through the dropping funnel. The mixture is reacted with reflux while taking out almost the by-produced water and further the reaction is continued with raising gradually the temperature while distilling off toluene from the system, by which there is obtained a viscous modified adduct (acid value: 23.0, total amine value: 0, remaining toluene: 3 % by weight).

The reaction product thus obtained (30 g), an epi-bis type epoxy resin derived from bisphenol A and epichlorohydrin (epoxy equivalent weight: 488) (70 g), ethylene glycol ethyl ether monoacetate (hereinafter, referred to as "EGA") (25 g), phenothiazine (0.25 g) and benzyltrimethylammonium chloride (10 mg) are reacted under nitrogen gas at 150°C for 3 hours, by which the acid value of the reaction system becomes zero (0). The liquid modified epoxy resin has an epoxy equivalent weight of 760 (converted as solid component) (calculated from the remaining epoxy groups thereof).

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The modified epoxy resin thus obtained was subjected to the following tests.

The liquid modified epoxy resin (10 g) was mixed well with diaminodiphenylmethane (0.53 g), and the mixture was coated onto a soft steel panel and was cured at 180°C for 20 minutes to give a cured film having excellent clarity and gloss. From the excellent clarity of the cured film, it was confirmed that the polybutadiene component had sufficient compatibility with the epoxy resin.

Besides, a cured film sample (thickness: 30 μ) prepared in the same manner as above showed a pencil hardness of H. When the surface of the sample was crosscut in checkerboard-like lines in squares of 1 mm x 1 mm and then the sample was bent by winding it around a column having a diameter of 4 mm so that the cut surface came outside, no change of the surface was observed. Besides, when a cellophane tape was adhered on the cut surface of the sample and thereafter was peeled off, neither peeling of the film nor relief was observed, by which it was confirmed that the cured film had sufficient flexibility and adhesion.

For comparison purpose, unmodified epi-bis type epoxy resin (epoxy equivalent weight: 488) (10.0 g), diaminodiphenylmethane (1.04 g) and EGA (2.5 g) were mixed well, and the mixture was coated onto a soft steel panel and cured likewise to give a colorless cured film having excellent gloss (thickness: 30 μ). This cured film showed a pencil hardness of H, but when it was crosscut in

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checkerboard-like lines likewise, the cured film was partially broken and peeled off, and further, by subjecting the cut surface to the bending test and to peeling off test with a cellophane tape, the cured film was wholly peeled
5 off.

Example 2

The same liquid polybutadiene as used in Example 1 (1280 g), maleic anhydride (320 g) and iron naphthenate (Fe: 5.0 %) (2.7 g) are charged into a 2 liter four-necked flask,
10 and the mixture is reacted under nitrogen gas at 190°C for 4 hours to give maleinated polybutadiene (total acid value: 218).

Into a 500 ml four-necked flask are charged the maleinated polybutadiene obtained above (250 g), butyl
15 cellosolve (15.3 g), 2,6-di-tert-butyl-4-methylphenol (hereinafter, referred to as "BHT") (2.5 g), toluene (67.0 g) and benzyldimethylamine (0.16 ml), and the mixture is reacted under nitrogen gas at 120°C for 2 hours, by which the acid value of the reaction system becomes 151. To the
20 reaction mixture is added a solution of cyclohexylamine (35.9 g) in toluene (35.6 g) through a dropping funnel while controlling the raising temperature due to exotherm below 130°C. With giving attention to occurrence of foaming, the temperature of the reaction mixture is gradually raised
25 until the final temperature becomes 180°C, during which the by-produced water and toluene are distilled off. When all materials having low boiling points are removed and the acid

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value of the reaction product becomes equilibrium at 24.7, the heating is stopped, by which there is obtained a viscous modified adduct (total amine value: 0, remaining toluene: less than 1 %).

5 The modified adduct thus obtained (200 g), an epi-bis type epoxy resin (epoxy equivalent weight: 488) (300 g), EGA (167 g) and benzyltrimethylammonium chloride (67 mg) are reacted under nitrogen gas at 150°C for 3 hours, by which the acid value of the reaction system becomes almost
10 zero (0). The liquid modified epoxy resin has an epoxy equivalent weight of 953 (converted as solid component) (calculated from the remaining epoxy groups thereof).

 When the liquid modified epoxy resin (267 g), EGA (28 g) and diethanolamine (22.0 g) are reacted under
15 nitrogen gas at 80°C for 3 hours, it is confirmed that the epoxy group is reacted. The epoxy resin containing an amino group obtained by the above reaction has a hydroxy group equivalent weight of 220 g/eq.

 To the epoxy resin containing amino group obtained
20 above is added dropwise a 70 % solution (137 g) of 2-ethylhexanol-semiblocked tolylene diisocyanate (2,4-bond/2,6-bond: 80/20 %) in EGA, and the mixture is reacted at 80°C for 2 hours to give a urethane-crosslinked type resin. The liquid resin thus obtained (450 g) is
25 neutralized with acetic acid (8.7 g) with stirring, and thereto is gradually added a deionized water (1440 g) to give a homogeneous electrocoating composition (pH 6.0) (This

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liquid composition is hereinafter referred to as "A composition").

A pigment paste is prepared as follows.

The A composition obtained above (100 g), titanium
5 oxide (rutile type) (72.9 g) and carbon black (5.9 g) are mixed with a paint conditioner for 30 minutes in order to disperse well the pigments.

To A composition (1790 g) is added with stirring
dibutyl tin dilaurate (1.6 g), and thereto is gradually
10 added the pigment paste obtained above (178.8 g) to give a homogeneous cationic electrocoating composition.

Example 3

The maleinated polybutadiene obtained in Example 2
(200 g), allyl alcohol (6.0 g), BHT (1.0 g), toluene (79 g),
15 benzyltrimethylammonium chloride (15 mg) and aniline (27.0 g) are reacted in the same manner as described in Example 1, by which the maleinated polybutadiene is semi-esterified with allyl alcohol and then imidated with aniline, during which the by-produced water and toluene are distilled off.
20 As a result, there is obtained a modified adduct (acid value: 24.9, total amine value: 0, remaining toluene: 3.5 % by weight, apparent viscosity at 60°C: 680 P).

The modified adduct thus obtained (150g), an
epi-bis type epoxy resin (epoxy equivalent weight: 488) (350
25 g), EGA (167 g) and benzyltrimethylammonium chloride (67 mg)
are reacted under nitrogen gas at 150°C for 3 hours, by

which the acid value of the reaction system become almost zero (0).

By using the liquid modified epoxy resin thus obtained, a urethane-crosslinked type resin is prepared in the same manner as described in Example 2, and further an electrocoating composition is prepared therefrom likewise.

Example 4

In the same manner as described in Example 2, maleinated polybutadiene and butyl cellosolve are reacted to give a reaction product (acid value: 151).

The reaction product is subjected to imidation of the remaining acid anhydride groups with p-aminophenol and aniline (1 : 2 by mole) likewise, during which the by-produced water and the solvent (toluene) are distilled off, by which there is obtained a viscous modified adduct (acid value: 24.8).

The modified adduct thus obtained (175 g) and an epi-bis type epoxy resin (epoxy equivalent weight: 488) (325 g) are reacted in EGA in the same manner as described in Example 2 to give a urethane-crosslinked type resin, and further an electrocoating composition is prepared therefrom likewise.

Reference Example 1

A mixture of an epi-bis type epoxy resin (epoxy equivalent weight: 490) (980 parts by weight) and methyl isobutyl ketone (297 parts by weight) are kept at 50 - 60°C, and thereto is added dropwise diethanolamine (210 parts by

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weight) over a period of 60 minutes, and the mixture is reacted for 60 minutes to give an amino group-containing epoxy resin.

To the resin thus obtained (660 parts by weight) is added dropwise the same semi-blocked tolylene diisocyanate as used in Example 2 (412.4 parts by weight), and the mixture is reacted at 80°C for 2 hours to give a urethane-crosslinked type resin (nonvolatile part: 70 %). The liquid resin thus obtained is neutralized with acetic acid with stirring and thereto is added a deionized water (3733.4 parts by weight) to give a homogeneous electrocoating composition (pH 6.0). By using this composition, a homogeneous cationic electrocoating composition is prepared in the same manner as described in Example 2. The composition has a nonvolatile part of 20 % and a pigment weight concentration of 20 %.

The cationic electrocoating compositions prepared in Examples 2, 3 and 4 and Reference Example 1 were subjected to electrocoating by using a steel plate treated with iron phosphate as a cathode and carbon plate as an anode at 30°C with stirring at 120 V for 3 minutes. After the electrocoating, the coated steel plate was washed with water, and cured at 180°C for 20 minutes to give a cured film having excellent gloss and gray color. Various properties of the test samples thus obtained were tested. The results are shown in Table 1.

Table 1

	Ex. 2	Ex. 3	Ex. 4	Ref. Ex. 1
Dispersibility of pigment	◎	◎	◎	◎
Thickness of film (μ)	20	20	20	20
Smoothness of the coating surface	◎	◎	◎	◎
Pencil hardness	4H	4H	4H	3H
Erichsen test	7.0mm	7.0mm	6.8mm	3mm
Erichsen, crosscut, peeling of tape *1	100/100	100/100	100/100	2/100
Bending resistance *2	◎	◎	◎	x
Impact resistance *3				
Surface	◎	◎	◎	x
Reverse	o	o	o	x
Salt spray test *4	◎	◎	◎	◎

[Remarks]: Evaluation was done as follows:

◎ : Excellent, o : Good, x : Bad

*1) The surface of the cured film was crosscut to form 100 squares (1 mm x 1 mm) in the same manner as described in Example 1. The samples were dipped into hot water at 50°C for 500 hours. After removal of the sample films from dipping bath, the wet surfaces of the sample films were wiped softly and air-dried. A cellophane tape was adhered on the surface of the sample film crosscut and was peeled off. The number of squared remained without being peeled off was counted, and the results are shown as the number of remained squared/100 (original number of squares).

*2) The test samples were bent by winding them around a column having a diameter of 2 mm, and the surface was observed.

5 *3) A load of 500 g was fallen on the test samples (on the coated surface or on the reverse side) from the height of 50 cm at a point of impact of 1/2", and the degree of damage of the coating film was observed.

10 *4) A 5 % saline (35°C) was sprayed onto the coated surface of the test samples for 1000 hours, and the degree of damage of the coated film was observed.

As is clear from the above test results, it was confirmed that the compositions of Examples 2, 3, and 4 of the present invention showed sufficient flexibility and adhesion and also excellent corrosion resistance.

15 Example 5

The modified adduct obtained in Example 2 (80 g), an epi-bis type epoxy resin (epoxy equivalent weight: 187) (120 g) and benzyltrimethylammonium chloride (20 mg) are reacted under nitrogen gas at 150°C for 2 hours to give a
20 pale yellow clear modified resin (acid value: 0, epoxy equivalent weight: 370, viscosity at 50°C: 10,000 cp).

The modified epoxy resin thus obtained (100 parts by weight) and diaminodiphenylmethane (25 parts by weight) are mixed, poured into a fixed mold and then cured under the
25 conditions of 80°C for 2 hours, 120°C for 2 hours, and 160°C for 2 hours in series.

The cured product thus obtained were subjected to Charpy impact test and also to a thermal shock test.

The thermal shock test was carried out as follows:

The epoxy resin composition was cured in an aluminum-made cup (diameter: 5 cm, height: 1.5 cm) wherein a bolt-nut washer was contained. The resulting cured product wherein the washer was embedded was taken out, and was subjected to heating-cooling cycle, i.e. repeating of heating at 100°C and then cooling at 0°C for each 30 minutes, and then, the number of the cycle until the sample was cracked was counted.

For comparison purpose, in the same manner as above except that an unmodified epi-bis type epoxy resin (epoxy equivalent weight: 187) was used instead of the modified epoxy resin, a cured test sample was prepared and subjected to the tests, likewise.

The results of the above tests are shown in Table 2.

Table 2

	Modified epoxy resin of the present invention	Unmodified epoxy resin
Charpy impact test	8.5 kg.cm/cm ²	4.5 kg.cm/cm ²
Thermal shock test (number of cycle)	More than 10 times	0 time

Example 6

A liquid polybutadiene (number average molecular weight: 600, viscosity at 30°C: 50 cp, iodine value: 450, cis-1,4 structure: 31 %, trans-1,4 structure: 64 %, and 1,2-vinyl structure: 5 %) (300 g), phenyl- α -naphthylamine (80 mg) and maleic anhydride (100 g) are charged into a 500

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ml four-necked flask, and the mixture is reacted under nitrogen gas at 190°C for 4 hours to give a maleinated polybutadiene (total acid value: 270).

5 Into a 500 ml four-necked flask are charged the maleinated polybutadine obtained above (200 g), BHT (1.0 g), allyl alcohol (10.9 g) and benzyldimethylamine (0.1 g), and the mixture is reacted at 90°C for 2 hours, and thereto is added dropwise aniline (30.0 g) through a dropping funnel. The mixture is reacted at 160°C for 3 hours while taking out
10 the by-produced water, by which there is obtained a viscous modified adduct (total amine value: 0, acid value: 44.8, viscosity at 60°C: 4,610 cp). It is confirmed that the acid anhydride groups in the maleinated polybutadiene are converted into semi-ester groups and imido groups by the
15 above analytical data and IR spectrum.

The modified adduct thus obtained (40 g) and an epi-bis type epoxy resin (epoxy equivalent weight: 488) (60 g) are reacted under nitrogen gas at 150°C for 3 hours to give a homogeneous modified epoxy resin being rich in
20 clarity (acid value: 0, epoxy equivalent weight: 1095).

The modified epoxy resin thus obtained was subjected to the following tests.

The modified epoxy resin (10 g), diaminodiphenylmethane (0.46 g) and EGA (30 g) were mixed well and the
25 resulting solution was coated onto a soft steel panel and cured at 180°C for 20 minutes to give a homogeneous clear cured film (pencil hardness: H).

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A cured coating film (thickness: 30 μ) was prepared likewise and crosscut in the same manner as described in Example 1, followed by subjecting to the bending test and peeling test of a cellophane tape likewise. As a result, no change of the coating surface and hence, it was confirmed that the coating film showed excellent flexibility and adhesion.

Reference Example 2

Into a 200 ml four-necked flask are charged a liquid polybutadiene containing terminal COOH group (molecular weight: 1450, acid value: 56, 1,2-vinyl bond: 91 %) (30 g), an epi-bis type epoxy resin (epoxy equivalent weight: 488) (70 g), EGA (34 g), BHT (0.5 g) and benzyl-trimethylammonium chloride (15 mg), and the mixture is reacted under nitrogen gas at 150°C for 3 hours to give a modified epoxy resin [acid value: almost 0, epoxy equivalent weight: 889 (converted as solid material)].

When the modified epoxy resin thus obtained was distilled under reduced pressure to remove the solvent, there was obtained a white opaque resin, by which it was assumed that the polybutadiene component of the resin was not sufficiently compatible with the epoxy resin. Besides, when the modified epoxy resin (10 g) was mixed with diaminophenylmethane (0.43 g), and the resulting mixture was coated onto a soft steel panel and cured at 180°C for 20 minutes, there was obtained an opaque coating film (thickness: 20 μ), from which the inferior compatibility was

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re-confirmed. Moreover, the surface of the coating film was somewhat shrunk, and when it was crosscut likewise, it showed blush and inferior adhesion by the peeling test of a cellophane tape.

5 Reference Example 3

The maleinated polybutadiene obtained in Example 1, i.e. 20 % by weight maleinated product of a liquid polybutadiene (number average molecular weight: 1680, cis-1,4 structure: 76 %) (80 g), toluene (20 g), ethylene glycol monobutyl ether (4.5 g), BHT (0.1 g) and
10 N,N-dimethylbenzylamine (50 mg) are reacted under nitrogen gas at 130°C for 1 hour to give a partially esterified product. The reaction mixture is heated to 70°C and thereto are added gradually N,N-dimethylpropane diamine (12.7 g) and
15 toluene (10 g), and the mixture is stirred at the same temperature for 1 hour. The mixture is heated until the final temperature becomes 170°C while taking out toluene and by-produced water to give a modified product (acid value: 23.0, total amine value: 72.0) (about 96 g).

20 The partially esterified-imidated product thus obtained (40 g), an epi-bis type epoxy resin (epoxy equivalent weight: 488) (60 g), EGA (42.8 g) and BHT (0.1 g) are reacted under nitrogen gas at 150°C for several tens of minutes, at when the reaction mixture shows suddenly
25 increased viscosity and finally gives an insoluble gel material. It is assumed that this phenomenon is due to ring-opening and polymerization of the large amounts of

epoxy groups which is catalyzed by the aliphatic tertiary amine having strong basicity bonded to the polybutadiene chain via imido bond, with proceeding of the reaction between carboxyl groups and epoxy groups.

- 5 From this reference example, it is clear that such diamine which remains a comparatively strong basic aliphatic amine nitrogen in the molecule can not be used as an imidating agent for the modifying process of the present invention wherein a part of the epoxy groups in epoxy resin
- 10 is modified and the remaining almost epoxy groups are remained in the free form for using them the subsequent reactions.

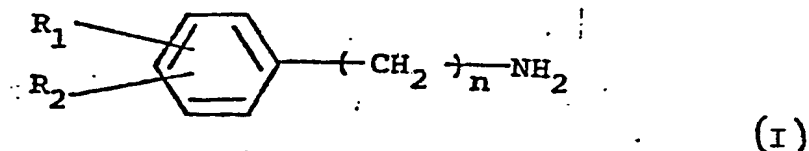
CLAIMS :

1. A modified epoxy resin composition, which comprises an epoxy resin and a modified adduct [D] of a conjugated diene polymer or copolymer which has an imido bond and/or amido bond and a semi-ester structure and has an acid value owing to a free carboxyl group of 5 to 100, the modified adduct being obtained by reacting an adduct A of a polymer of a conjugated diene having a number average molecular weight of 300 to 20,000 or a copolymer of the conjugated diene and a vinyl monomer with an α,β -unsaturated dicarboxylic acid or its anhydrides, with a compound [B] containing one primary amino group in the molecule and a compound [C] containing a hydroxy group in the molecule.

2. A modified epoxy resin composition as claimed in Claim 1 wherein the conjugated diene monomer is butadiene, isoprene, chloroprene or 1,3-pentadiene, and the vinyl monomer is an acrylic acid ester, a methacrylic acid ester, acrylonitrile, styrene, acetylene, ethylene or propylene.

3. A modified epoxy resin composition as claimed in Claim 1 or Claim 2 wherein the α,β -unsaturated dicarboxylic acid is maleic anhydride, maleic acid, fumaric acid, itaconic acid or citraconic acid.

4. A modified epoxy resin composition as claimed in any one of the preceding claims wherein the compound [B] containing one primary amino group is a compound of the formula :



wherein R_1 and R_2 are the same or different and are each hydrogen, an alkyl group having 1 to 5 carbon atoms, halogen, cyano, hydroxy, thiol, methoxy, $-\text{CONH}_2$, $-\text{COCH}_3$, $-\text{COOCH}_3$, or $-\text{N}(\text{CH}_3)_2$, and n is 0 or an integer of 1 to 3.

5. A modified epoxy resin composition as claimed in any one of claims 1 to 3 wherein the compound [B] containing one primary amino group is a compound of the formula:



wherein R_3 is an aliphatic hydrocarbon group having 1 to 18 carbon atoms or an alicyclic hydrocarbon group having 3 to 18 carbon atoms, the aliphatic and alicyclic hydrocarbon groups optionally containing an ether bond.

6. A modified epoxy resin composition as claimed in any one of the preceding claims wherein the compound [c] containing a hydroxy group is a compound of the formula :



wherein R_4 is a saturated or unsaturated hydrocarbon group having 1 to 18 carbon atoms; a saturated or unsaturated hydrocarbon group having 1 to 12 carbon atoms and containing a cyano group, a halogen atom, an ether bond, an ester bond or a hydroxy group which bonds to a secondary or tertiary carbon; a saturated alcohol residue having 1 to 8 carbon atoms; an acrylic acid residue; or a methacrylic acid residue- and m is 0 or an integer of from 1 to 3.

7. A modified epoxy resin composition as claimed in any one of the preceding claims wherein the epoxy resin contains at least one epoxy group.

8. A modified epoxy resin composition as claimed in any one of the preceding claims wherein the modified adduct [D] is used in an amount of from 5 to 300 parts by weight to 100 parts by weight of the epoxy resin.

9. A process for producing a modified epoxy resin composition which comprises reacting or mixing an epoxy resin with at least one modified adduct [D] of a conjugated diene polymer or copolymer which has an imido bond and/or amido bond and a semi-ester structure and has an acid value owing to a free carboxyl group of 5 to 100, the

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modified adduct being obtained by reacting an adduct [A] of a polymer of a conjugated diene having a number average molecular weight of 300 to 20,000 or a copolymer of the conjugated diene and a vinyl monomer with an α, β -unsaturated dicarboxylic acid or its anhydride, with a compound [B] containing one primary amino group in the molecule and a compound [C] containing a hydroxy group in the molecule.

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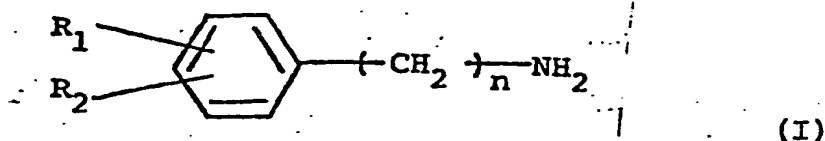
CLAIMS :

1. A process for producing a modified epoxy resin composition which comprises reacting or mixing an epoxy resin with at least one modified adduct [D] of a conjugated diene polymer or copolymer which has an imido bond and/or amido bond and a semi-ester structure and has an acid value owing to a free carboxyl group of 5 to 100, the modified adduct being obtained by reacting an adduct [A] of a polymer of a conjugated diene having a number average molecular weight of 300 to 20,000 or a copolymer of the conjugated diene and a vinyl monomer with an α, β -unsaturated dicarboxylic acid or its anhydride, with a compound [B] containing one primary amino group in the molecule and a compound [C] containing a hydroxy group in the molecule.

2. A process as claimed in Claim 1 wherein the conjugated diene monomer is butadiene, isoprene, chloroprene or 1,3-pentadiene, and the vinyl monomer is an acrylic acid ester, a methacrylic acid ester, acrylonitrile, styrene, acetylene, ethylene or propylene.

3. A process as claimed in Claim 1 or Claim 2 wherein the α, β -unsaturated dicarboxylic acid is maleic anhydride, maleic acid, fumaric acid, itaconic acid or citraconic acid.

4. A process as claimed in any one of the preceding claims wherein the compound [B] containing one primary amino group is a compound of the formula :



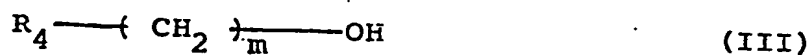
wherein R_1 and R_2 are the same or different and are each hydrogen, an alkyl group having 1 to 5 carbon atoms, halogen, cyano, hydroxy, thiol, methoxy, $-\text{CONH}_2$, $-\text{COCO}_3$, $-\text{COOCH}_3$, or $-\text{N}(\text{CH}_3)_2$, and n is 0 or an integer of 1 to 3.

5. A process as claimed in any one of claims 1 to 3 wherein the compound [B] containing one primary amino group is a compound of the formula :



wherein R_3 is an aliphatic hydrocarbon group having 1 to 18 carbon atoms or an alicyclic hydrocarbon group having 3 to 18 carbon atoms, the aliphatic and alicyclic hydrocarbon groups optionally containing an ether bond.

6. A process as claimed in any one of the preceding claims wherein the compound [C] containing a hydroxy group is a compound of the formula:



wherein R_4 is a saturated or unsaturated hydrocarbon group

having 1 to 12 carbon atoms and containing a cyano group, a halogen atom, an ether bond, an ester bond or a hydroxy group which bonds to a secondary or tertiary carbon; a saturated alcohol residue having 1 to 8 carbon atoms; an acrylic acid residue; or a methacrylic acid residue; and m is 0 or an integer of from 1 to 3.

7. A process as claimed in any one of the preceding claims wherein the epoxy resin contains at least one epoxy group.

8. A process as claimed in any one of the preceding claims wherein the modified adduct [D] is used in an amount of from 5 to 300 parts by weight to 100 parts by weight of the epoxy resin.



European Patent
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EUROPEAN SEARCH REPORT

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Application number

EP 81 30 6181.9

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	DE - A1 - 3 000 911 (SUMITOMO CHEMICAL CO. LTD.) * claims 1, 2, 5; page 7, line 4 to page 11, line 2 * & US - A - 4 294 940 --	1-3, 5-9	C 08 G 59/14
P,A	Patent Abstracts of Japan Vol. 5, No. 8, 20 January 1981	1,2	
A	& JP - A - 55 - 137125 (25.10.80) --		TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
A	Chemical Abstracts vol. 92, no. 22 2 June 1980 Columbus, Ohio, USA H. NAKADA et al. "Cationic polymer electrophoretic coating materials" page 74, column 1, abstract no. 182638u	1	C 08 G 59/00 C 09 D 5/40
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A	Chemical Abstracts vol. 92, no. 22 2 June 1980 Columbus, Ohio, USA H. NAKADA et al. "Cationic polymer electrophoretic coating materials" page 74, column 2, abstract no. 182639v		CATEGORY OF CITED DOCUMENTS
D,A	& JP - A - 80 - 05933 (KANSAI PAINT CO. LTD.), 17 January 1980 ----		X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 23-03-1982	Examiner IDEZ

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